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HYDROSTATIC EFFECT IN A BINARY SOLUTION NEAR THE CRITICAL DISSOLUTION POINT

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The question of the existence of the theoretically-predicted [1, 2] hydrostatic effect near the critical lamination point of a solution has been under discussion in recent years. According to [1, 2], the concentration gradient over the height of a column of liquid is $dx/dH \sim (\partial\mu/\partial x)_{P,T}^{-1}$. If $(\partial^3\mu/\partial x^3)_{P,T} \neq 0$ at the critical point, then it follows that at the critical point the height variation of the concentration is given by $x - x_k = \Delta x \sim (H - H_0)^{1/3}$, where H_0 is the position of the lamination solution line [2].

Using the Toepler method, we investigated the distribution of the concentration in a binary CH_4 - CF_4 solution having an upper critical mixing point ($T_c = 94.72^\circ K$; $x_c = 43.5\% CF_4$). The connection between the experimentally-determined gradient of the refractive index and the concentration gradient was obtained by using the Lorenz-Lorentz equation. The refractive indices of the components were taken from [4]. The critical-concentration solution was investigated in a previously-described cryostat [5], with a thermostat accuracy $\pm 0.001^\circ K$.

The solution was stirred at temperatures above T_c until it became completely homogeneous. The degree of homogeneity was monitored against the shadow picture; the solution was then kept at a thermostatically controlled temperature until the variation of the concentration gradient stopped completely. As a result, inhomogeneities of the composition along the height of the liquid column were observed. The time required to reach equilibrium depended on the degree of approach to T_c , and reached 50 - 70 hours at $T - T_c = \Delta T \sim 1^\circ K$; it increased sharply with decreasing ΔT . At $\Delta T \sim 0.2^\circ K$, no equilibrium was reached even after about 300 hours.

The measurements were performed either in the presence of a "vapor-liquid" interface inside the chamber or with the chamber completely filled with liquid, with a meniscus in the supply capillary entering the lateral part of the chamber. In the former case, a concentration gradient was produced near the surface of the liquid immediately after stirring. The surface layers became richer in methane, the enrichment increasing the closer the temperature to critical. The thickness of these layers reached 1 - 10 mm and also increased on approaching T_c . In addition, drops of liquids enriched with the heavy component were precipitated from the surface layer (they could be seen only on the shadow picture). The rate of drop formation increased on approaching the lamination point, and led to the occurrence of a concentration gradient even in the lower part of the chamber. As time went on, the process of drop formation stopped and the concentration in the lower part of the chamber became equalized, while a concentration gradient still remained in the surface layer. The described effects were observed in a temperature interval up to $\Delta T \sim 16^\circ K$ above critical.

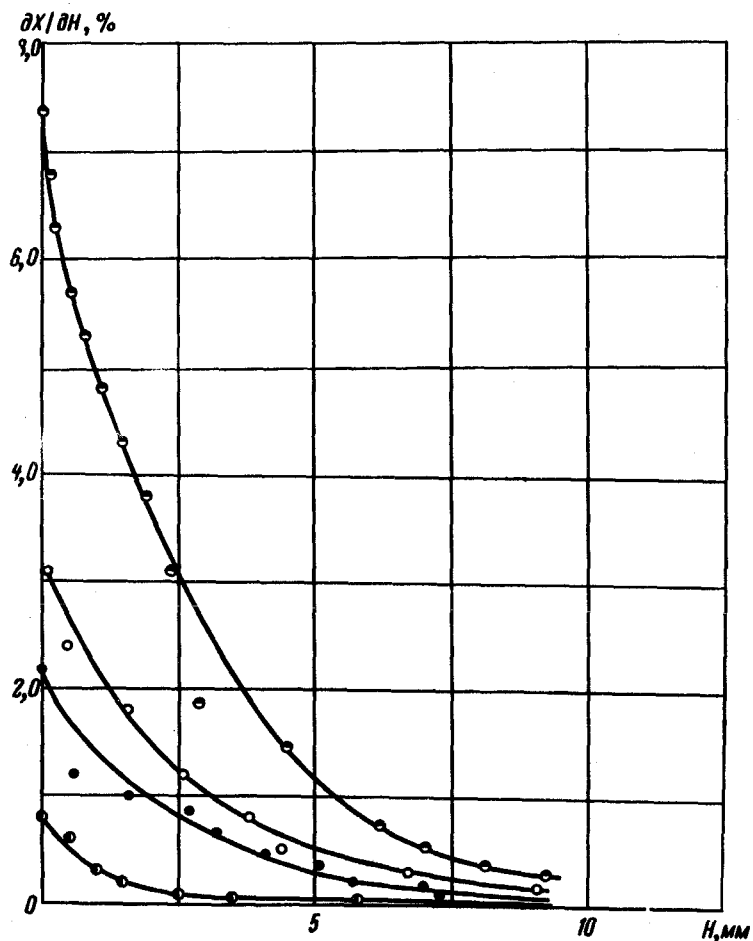


Fig. 1. Concentration gradient dx/dH vs. distance H to the surface of the liquid at $T > T_c$:
 ● - $\Delta T = 0.790^\circ\text{K}$, ○ - 4.785°K ,
 ● - 7.335°K , ● - 16.740°K .

Figure 1 shows the dependence of the concentration gradient on the distance to the surface of the liquid H , at different ΔT . We see that the maximum concentration gradient occurs at the surface of the liquid and decreases rapidly with increasing distance from the surface. The obtained concentration distribution over the height H is approximately exponential, $\Delta x = \Delta x_0 \exp(-\alpha H)$, where α is a function of the temperature and decreases on approaching T_c , corresponding to an increase of the effective thickness of the surface layer in which the change of concentration is observed. In the case when there was no vapor phase in the chamber, the described effects were not observed, and the solutions remained homogeneous at the corresponding temperatures.

At temperatures below T_c , after the stirring was stopped and the turbidity due to the dispersion of the system disappeared, a growing concentration gradient occurred at the interface between the two liquid phases. In analogy with the case when a vapor phase was present in the chamber at $T > T_c$, a concentration gradient was produced in the surface layer, but its magnitude was much smaller. The time of establishment of the equilibrium distribution depended on the proximity to the critical point, and reached several dozen hours. Figure 2 shows the obtained plots of dx/dH against H for different temperatures. The interface between the liquid phases lies at the vertices of the peaks for all curves of the figure. For a qualitative comparison of the experimental data with theory [2], Fig. 3 shows a plot of dx/dh against $h = H - H_0$ for $|\Delta T| = 0.031^\circ\text{K}$ in a log-log scale. Owing to the noticeable diffuseness of the phase boundary, the value of H_0 could not be determined with sufficient accuracy, and it was chosen such as to make the lines corresponding to two different branches

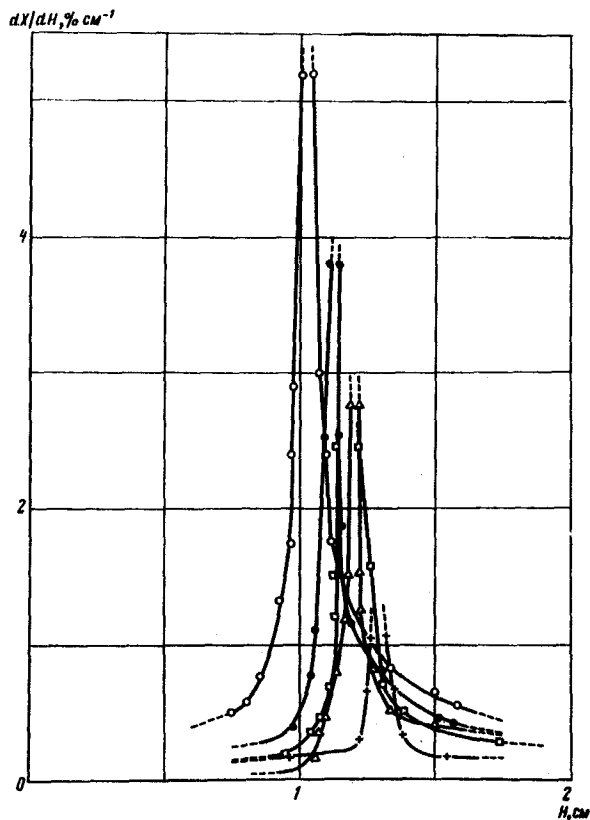


Fig. 2. Distribution of the concentration gradient of methane, dx/dH , over the height of the chamber, H , at $T < T_c$: \circ - $\Delta T = 0.031^\circ K$, \bullet - $0.038^\circ K$, \square - $0.046^\circ K$, Δ - $0.060^\circ K$, $+$ - $0.070^\circ K$.

of the curve parallel. We see that the observed dependence has the form $dx/dh = ah^{-n}$ with $n = 0.78$, and then $\Delta x = a'h^{1-n}$, where the exponent $1 - n = 0.22$ is close to 0.2. The latter value can be obtained within the framework of the theory [2], provided the first nonzero derivative at the critical point is the fifth derivative of the chemical potential with respect to the concentration.

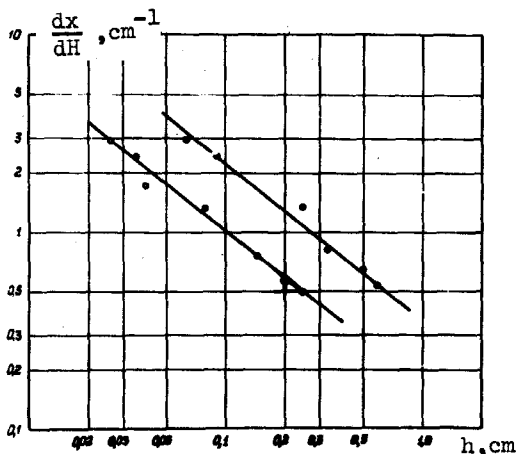


Fig. 3. Concentration gradient dx/dH of methane vs. the distance h to the lamination line ($\Delta t = 0.031$): \circ - $H < H_0$, \bullet - $H > H_0$.

Thus, the experimental results apparently offer evidence that the obtained distribution of the concentration of the solution below T_c is due to the action of the gravitational field and constitutes the hydrostatic effect predicted in [2]. This raises the question why the effect was not observed at $T > T_c$ in a completely filled chamber. The possible reasons are, first, the fact that the investigation was carried out in a temperature interval farther from T_c (minimal $\Delta T = 0.790^\circ K$), and second, the rate of approach to the equilibrium distribution

was too slow. If this process proceeds via diffusion, then its characteristic time is $\tau \sim \ell^2/D$, where ℓ is in this case the height of the chamber, ~ 5 cm. For our system at $\Delta T \approx 0.1 - 1^\circ\text{K}$, we have $D \sim 10^{-7}$ cm²/sec, hence $\tau \sim 2.5 \times 10^8$ sec ~ 10 years, i.e., a time greatly exceeding the experimental possibilities. In measurements below T_c , the main effect is observed in a layer of ~ 1 cm near the separation boundary, and D can be higher because both phases are far from the critical concentration. At $D \approx 10^{-6}$ cm²/sec we obtain $\tau \sim 10^6$ sec ~ 300 hours, i.e., a feasible experiment time of the same order as the time required to approach equilibrium in our investigations.

The occurrence of a concentration gradient in the surface layer at $T > T_c$ cannot be readily attributed to a simple growth of the absorption layer near the critical point, since the thickness of the layers is in this case larger by several orders of magnitude than the known values [6]. It is possible that the effect is the result of a simultaneous action of gravitational and surface forces. The most natural explanation of the process of drop formation in the surface layer is the assumption of surface lamination of the solution [7], occurring in the initial time interval prior to establishment of equilibrium of the concentration distribution.

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EXCITATION OF SRS IN LIQUIDS UPON Q SWITCHING OF A LASER BY THE INVESTIGATED SUBSTANCE

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To excite stimulated Raman scattering (SRS) it is customary to use a laser having a special device for Q switching. In the present investigation we obtained powerful SRS in a number of organic liquids by excitation with a ruby laser whose Q-switching was effected by the investigated substance itself. The employed Q-switching method is based on exciting in the medium a backward stimulated Mandel'shtam-Brillouin scattering (SMBS), leading to reflection of an appreciable fraction of the incident radiation towards the laser. The method was proposed earlier in [1], where a giant pulse was obtained by using CS₂, in which intense SMBS can be easily excited¹).

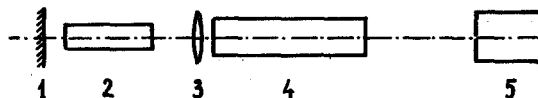


Fig. 1. Experimental setup.

¹) Somewhat different conditions for the formation of a giant pulse in backward SMBS were used in [2], where powerful nanosecond SRS pulses were obtained in compressed nitrogen.